The Separation of Cobalt and Copper from other Metals by Phenylthiohydantoic Acid and the Volumetric Determination of Cobalt

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By

Helen Dorothy Hall

1920

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HELEN DOROTHY HALL

Ann Arbor, Mich.
February, 1920

THE SEPARATION AND DETERMINATION OF COBALT. I. THE SEPARATION OF COBALT BY MEANS OF PHENYL-THIOHYDANTOIC ACID

Part I. Separation of Cobalt from Other Metals

Introduction

The present methods for the separation and determination of cobalt leave much to be desired in respect to accuracy and rapidity. Especially is there need of some reagent which will separate it from a large number of other metals. Nitroso-β-naphthol is widely used for this purpose, but it also precipitates iron, one of the metals most commonly associated with cobalt. Pozzi-Escot[1] suggested as a qualitative test for cobalt its precipitation from ammoniacal solution by the monosubstitution products of the thiohydantoic acids, particularly phenyl- or β-naphthyl-hydantoic acid; cobalt gives a purplish-red precipitate and nickel a brown one, the latter being soluble in concentrated ammonia, thus making possible the detection of cobalt in the presence of nickel. As a qualitative reagent phenyl-thiohydantoic acid was introduced into this laboratory some years ago. It seemed desirable, therefore, to study its use as a quantitative reagent, and since the precipitate thus obtained cannot be weighed directly it was necessary to investigate the gravimetric and volumetric methods of determining cobalt, the report of which will appear in subsequent papers.

Phenyl-thiohydantoic acid precipitates cobalt quantitatively in slightly ammoniacal solution. The compound varies somewhat in color; it is usually brownish- or purplish-red and is readily filtered and washed, especially when hot. The precipitate contains a large amount of water and shrinks enormously in volume when dried. By means of this reagent, cobalt may be completely separated from aluminum, chromium, vanadium, uranium, tungsten, molybdenum, arsenic, titanium, zinc, manganese, calcium and magnesium, while iron is carried down only to a very slight extent. Nickel is partially precipitated and the precipitate is soluble in concentrated ammonia. It is, however, impossible to add much concentrated ammonia without interfering with the precipitation of cobalt. Most metals of the hydrogen sulfide group are precipitated. The various separations will be described in detail.

[1] Pozzi-Escot, *Ann. chim. anal. chim. appl.*, **10**, 147 (1905).

Preparation of Materials

Phenyl-thiohydantoic acid, $C_6H_5NC(NH_2)SCH_2COOH$, was prepared by the method of Nencki and Jaeger.[2] The procedure is as follows.

To a mixture of 189 g. of monochloro-acetic acid and 152 g. of ammonium thiocyanate in a round-bottom flask are added 186 g. of aniline and 930 cc. of ethyl or methyl alcohol. The mixture is heated under a reflux condenser on the water-bath for several hours, after which the undissolved part is allowed to settle and the clear, brown-yellow liquid is poured into a large evaporating dish. It is allowed to cool, whereupon crystallization takes place. Sometimes the liquid crystallizes slowly, probably because of impurities. Stirring then often hastens crystallization. The yellow crystals are filtered on a Büchner funnel, washed with water and dried. The product is recrystallized from alcohol and then from water. By further refluxing the mother liquor with the undissolved part from which the liquid was decanted, a second crop of crystals may be obtained. A 60–70% yield is possible.[3]

Phenyl-thiohydantoic acid crystallizes in flat plate-like crystals, which are perfectly white when pure. As usually prepared, it possesses a characteristic odor which is much decreased by recrystallization from water.

The solubility in 100 cc. of water at 100° was found to be about 10 g. and at 20° less than 1 g.; that in alcohol is similar, but the acid is much more soluble in acetone. A saturated aqueous or alcoholic solution may be used as a reagent. If this is too dilute, acetone may be used or the solid dissolved in hot water when needed.

The cobalt used was in the form of metallic cobalt, which was prepared by electrolysis from chloropentammine cobaltic chloride, the form in which cobalt is most readily purified.

To a cold solution of 50 g. of cobalt chloride, "nickel free," (containing 25.8% of cobalt) and 100 g. of ammonium chloride in 300 cc. of conc. ammonia (sp. gr. 0.90), 25 cc. of 30% hydrogen peroxide solution was added at once, then 2 or 3 cc. at a time, until 50 cc. had been added. Other oxidizing agents were less satisfactory since larger amounts of the other amines were formed. After the oxidation was complete the solution was neutralized with conc. hydrochloric acid and 50 cc. excess added, after which the solution was heated to boiling and allowed to cool. The purple precipitate was filtered off and dissolved in a 2% ammonia solution, filtered hot, acidified with hydrochloric acid and boiled. Practically the theoretical yield of amine was obtained. The purity of the original cobalt chloride was shown by the fact that the mother liquors from the precipitation of the chloropentammine salt contained only a trace of nickel.

The chloropentammine chloride was dissolved in ammonia and electrolyzed by a current of 2 amperes for 24 hrs. The cathode was a piece of platinum foil covered with a thin film of vaseline. The cobalt deposit was then peeled off as a sheet and ignited in hydrogen at a bright red heat to reduce any oxide or chloride that might have been occluded. To make sure of the purity of the cobalt, weighed amounts were dissolved in nitric acid, evaporated with sulfuric acid to dryness and ignited in a muffle furnace at 550° until constant weight was obtained, which required

[2] Nencki and Jaeger, *J. prakt. chem.*, [2] **16,** 17 (1877).

[3] This reagent is now obtainable from the Eastman Kodak Company.

about 2 ignitions of 1 hour each. Previous work[4] showed that above this temperature the sulfate slowly decomposes.

The cobalt sulfate thus formed dissolved clear in water and was neutral. The following results were obtained.

TABLE I

ANALYSES OF METALLIC COBALT

Co taken G.	$CoSO_4$ found G.	Co found G.	Error Mg.
0.1329	0.3500	0.1332	+0.3
0.0211	0.1869	0.0211	0.0
0.1009	0.2649	0.1008	−0.1
0.1212	0.3181	0.1211	−0.1

Method of Precipitation

Amounts of metallic cobalt equivalent to about 25 mg. were used for each determination. For every 25 mg. of cobalt 0.7 to 1 g. of phenyl-thiohydantoic acid dissolved in 30 cc. of water or alcohol was added to the hot ammoniacal cobalt solution in a volume of 200–300 cc. After boiling for a few seconds with constant stirring, the precipitate separated at the top so that it was possible to detect any pink color in the clear solution, indicating incomplete precipitation. Unless the solution is distinctly alkaline, precipitation will be incomplete. The least amount of ammonia which will induce complete precipitation is 1 cc. (sp. gr. 0.90) in a volume of 300 cc., but as much as 10 cc. may be present without interference. With 20 cc., however, precipitation is again not quite complete. Continuous stirring or shaking tends to hasten the process. The bulky precipitate was washed with hot water and then dried, whereupon it shrank to a convenient size and was easily ignited to the oxide.

Composition of the Precipitate

Various experiments were tried to ascertain the composition of the cobalt precipitate. From the amount of reagent required to give complete precipitation, no definite information could be obtained. The smallest amount of reagent that would completely precipitate 25 mg. of cobalt was 400 mg., or 16 times the weight of the metal.

Cobalt sulfate and chloropentammine cobalt chloride were precipitated with phenyl-thiohydantoic acid and the precipitates dried in a vacuum desiccator over sulfuric acid for 3 days. Samples of these were weighed, ignited, fused with potassium pyrosulfate, dissolved and the cobalt determined volumetrically, as described later. Using the same material the percentage of cobalt found varied from 9.1% to 11.6% and the 2 preparations were essentially alike, although they were precipitated from salts of bivalent and trivalent cobalt, respectively. The average value was 9.9%, while the theoretical percentage for bivalent cobalt is 12.3

[4] By Mr. R. D. Smith.

and for trivalent, 8.6. One determination of sulfur gave 17.86% as compared with a theoretical value of 13.2%, assuming the formula $(C_9H_9O_2N_2S)_2Co$. It is obvious that the precipitate is contaminated with sulfide or some other sulfur compound, as might be expected from the varying color of the different precipitates. Therefore, the precipitate cannot be weighed directly.

Separation of Iron

Iron and cobalt are usually separated by precipitating the iron as the basic acetate[5] or as hydroxide by adding zinc oxide or some similar neutralizing agent.[6] Iron may be separated by shaking out with ether,[7] but usually traces of cobalt remain in the ether extract. Cobalt may be extracted from a solution containing thiocyanate by means of a mixture of ether and amyl alcohol; sodium pyrophosphate is added to retain the iron in the water solution.[8] There is, however, no reagent which precipitates cobalt and separates it completely from iron.

Phenyl-thiohydantoic acid may be used to separate cobalt from iron. The latter does not precipitate in the presence of citrate, although very small amounts are carried down each time when cobalt is present, the exact amount depending on the conditions of precipitation. Vigorous agitation of the solution is necessary as soon as the reagent has been added and before the cobalt begins to precipitate. If the cobalt precipitate is red, then the proper procedure for precipitation has been followed and very little iron will be found with the cobalt; but if a black precipitate forms (probably due to the presence of ferrous sulfide) it may contain as much as 50 mg. of iron and must be discarded. Small amounts of iron will cause no trouble unless gravimetric methods are used in the final determination of the cobalt.

To determine whether precipitation was complete the precipitate was filtered off, and to the filtrate more of the reagent was added. The second precipitate, consisting mainly of the reagent with a little iron, was ignited, fused with potassium hydrogen sulfate, dissolved in water and tested for cobalt with nitroso-β-naphthol in ammoniacal citrate solution by the method of Atack[9] modified by Jones.[10] Since 0.01 mg. of cobalt gives a deep red color, it was possible by using a standardized solution to estimate quite closely the amount of cobalt present.

The most satisfactory removal of cobalt from iron was obtained by the following method, using a 500cc. Erlenmeyer flask. The total volume of the solution was kept at about 300 cc. The solution, containing 25 mg. of cobalt, 1 g. of iron in the form of ferric alum, and 8 g. of citric acid,

[5] McIntosh, *Chem. News*, **56**, 64 (1887). Hare, *J. Am. Chem. Soc.*, **17**, 537 (1895). Campbell, *Z. anal. Chem.*, **30**, 616 (1893).

[6] Vortman, *Jahresber.*, **1894**, 2534. Slavik, *Chem.-Ztg.*, **38**, 514 (1914).

[7] Brunck, *Chem.-Ztg.*, **37**, 1374 (1913).

[8] Rosenheim and Huldschinsky, *Ber.*, **34**, 2050 (1901).

[9] Atack, *J. Soc. Chem. Ind.*, **34**, 64 (1915).

[10] Jones, *Analyst*, **43**, 317 (1918).

was neutralized with ammonia (sp. gr. 0.90) and 5 cc. excess was added. To the warm solution (35°) was added 0.7 to 1.0 g. of phenyl-thiohydantoic acid dissolved in 30 cc. of water or alcohol. The flask was quickly stoppered and shaken for several minutes. The cobalt precipitated at once, and when heated to boiling for several minutes it filtered easily. The filtrate was tested for complete precipitation of the cobalt, as described above. After washing with 0.5% ammonium citrate solution until the wash water gave no test for iron, the precipitate was dried, ignited, and then fused with potassium pyrosulfate. The fused mass was then dissolved in water, diluted to 200 cc., and 10 g. of ammonium chloride added. The iron was precipitated twice by adding dil. ammonia to the hot solution, ignited to oxide, and weighed as such. Proceeding as indicated above, and adding 1 g. of reagent, the amount of iron precipitated varied irregularly in 20 experiments from a trace to 9. mg., the average being 3.7 mg. Cobalt was completely precipitated in all cases.

When only 0.7 g. of reagent was added, the minimum amount required for complete precipitation in the presence of 1 g. of iron, somewhat less of the latter was precipitated the amounts varying from 2.1 to 4.5 mg. with an average of 2.9 mg. With 10 mg. of iron present in 2 experiments, 1.0 and 2.3 mg. were precipitated. The presence of nickel still further decreases the amount of iron precipitated, probably because in this case the precipitate is more finely divided and easier to wash, but the iron rarely falls below 1.5 mg. The reason for this effect of adding a large excess of the reagent is doubtless because the excess crystallizes out on cooling slightly even though the solution is filtered hot, and these crystals carry iron.

If instead of a flask a 600cc. beaker is used for the precipitation, the separation is not as good, since the agitation of the solution is more difficult. When precipitated under such conditions the reagent was added to the boiling solution and boiling was continued for a few minutes. The amount of iron in the precipitate varied from 3 to 10 mg., the average being 8 mg., and even when precipitated twice it varied from 2 to 6 mg.

The only objection to using an Erlenmeyer flask is the difficulty of removing the precipitate, for usually the last trace cannot be transferred; but the precipitate is so bulky that the slight amount adhering to the flask is negligible.

In the following experiments cobalt was precipitated in the presence of 1 g. of iron as described above, and then determined volumetrically

Table II

Precipitation of Cobalt in the Presence of Iron

Co taken G.	Co found G.	Error Mg.
0.0321	0.0319	−0.2
0.0245	0.0250	+0.5
0.0238	0.0241	+0.3
0.0270	0.0265	−0.5
0.0306	0.0303	−0.3
0.0337	0.0339	+0.2

by oxidation to cobaltic hydroxide and reduction with titanous sulfate as outlined later.

Precipitation in the Presence of Nickel

The literature on the subject of the separation of nickel and cobalt is extensive, but since the method used here is not a separation of these 2 elements, no other methods will be discussed. Nickel is precipitated by phenyl-thiohydantoic acid under the same conditions as is cobalt, but not quantitatively. Nickel forms a brown precipitate which is soluble in hot dil. ammonia to a certain extent and is completely soluble in hot conc. ammonia. It would be impossible, however, to remove the nickel with hot conc. ammonia without affecting the cobalt precipitate, nor can the precipitated nickel be dissolved with hot alcohol.

In the presence of more than 20 cc. of ammonia (sp. gr. 0.90), complete and immediate precipitation of cobalt is not possible. The following results show the effect of adding more ammonia during precipitation.

TABLE III

EFFECT OF ADDITION OF AMMONIA

Ammonia added (Sp. gr. 0.90) Cc.	Ni added Mg.	Ni in ppt. Mg.
50	19	6.0
16	19	9.0
10	19	7.2
10	10	9.4
10	5	1.4

In the presence of 1 g. of iron and 19 mg. of nickel the amount of iron in the precipitate varied from 0 to 5.5 mg., the average being 2.8 mg. The addition of more nickel had no effect. When only 5 mg. of iron was present 0.8 mg. was carried down; 0.7 g. of reagent was used in these experiments.

TABLE IV

NICKEL AND IRON IN PRECIPITATE

Ni added Mg.	Ni in ppt. Mg.	Fe added G.	Fe in ppt. Mg.
9.5	4.2	1	4.2
19.0	3.9	1	2.6
19.0	9.0	0.01	0.9
19.0	6.7	0.008	0.8
19.0	12.0	0.004	0.8
38.0	11.4	1	3.8
50.0	11.9	1	2.5
50.0	9.0	...	...
60.0	14.0	...	...

The amounts of both nickel and iron carried by the precipitate were determined in the following experiments, 0.7 g. of phenyl-thiohydantoic acid being used in each case. These precipitates were washed with hot

0.5% ammonium citrate solution until the wash water gave no test for iron or nickel. It was noticed that the filtrate immediately after the filtration of the cobalt gave no test for nickel with dimethylglyoxime, but as soon as washing of the precipitate was started nickel began to precipitate. This shows that nickel is precipitated with the cobalt and by washing is partially removed. When the volume during precipitation was increased to 700 cc. no improvement was apparent.

Separation from Zinc

Cobalt is usually separated from zinc by precipitation with nitroso-β-naphthol; zinc may be separated from cobalt by precipitation as sulfide from a solution slightly acid with formic or monochloro-acetic acid,[11] or containing the cobalt as cobalticyanide.[12]

Experimental.—Cobalt was completely separated from zinc in one precipitation by phenyl-thiohydantoic acid. The solution, 400 cc. in volume, contained citrate and 10 cc. of ammonia (sp. gr. 0.90) in excess. The reagent was added to the boiling cobalt solution and the boiling continued for several minutes. Zinc has a very noticeable effect in retarding the precipitation of cobalt, but by keeping the solution warm and stirring frequently all of the cobalt was precipitated in $^1/_2$ hour, and a clear, colorless filtrate left. The cobalt precipitate was washed with hot 0.5% ammonium citrate 15 times and then dried. After burning off the carbon, the cobalt oxide was fused with potassium pyrosulfate, the fused mass dissolved in water, the solution diluted to 200 cc. and tested for zinc by passing hydrogen sulfide into the hot, slightly acid solution. No test for zinc could be obtained.

Separation from Manganese

Funk's method[13] of separating cobalt from manganese is based on the fact that manganous sulfide is soluble in formic acid and acetic acid. He was also able to separate cobalt from very small amounts of manganese by precipitation as potassium cobaltinitrite.[12] One of the best methods is precipitation of the cobalt with nitroso-β-naphthol.

Experimental.—The same conditions of precipitation were used as for the separation from iron. Precipitation was complete at once. After washing, the precipitate was dried, ignited and fused with potassium pyrosulfate. Manganese was tested for by oxidation to permanganate with potassium periodate,[14] using a blank to make sure of the color change. No trace of manganese could be detected.

Separation from Other Metals

By precipitating cobalt in a volume of 400 cc. with 7 g. of citric acid and 10 cc. excess of ammonia (sp. gr. 0.90) complete separation from arsenic, titanium, uranium, vanadium, tungsten, molybdenum, aluminum, chromium, calcium and magnesium was accomplished in one precipitation. The cobalt was not determined, but the precipitate was entirely

[11] (a) Berg, *Z. anal. Chem.*, **25,** 512 (1886). (b) Rosenheim and Huldschinsky, *Z. anorg. Chem.*, **32,** 84 (1902).

[12] Funk, *Z. anal. Chem.*, **46,** 1 (1907). Ref. 12 b.

[13] Funk, *ibid.*, **45,** 562 (1906).

[14] Willard and Greathouse, *J. Am. Chem. Soc.*, **39,** 2366 (1917).

free from the other metals present. The precipitate was sometimes a little slow in forming, but when the solution was boiled, frequently stirred and allowed to stand, complete precipitation and separation were always obtained.

Summary

1. Cobalt may be quantitatively separated in one operation from arsenic, uranium, vanadium, titanium, tungsten, molybdenum, zinc, manganese, chromium, aluminum, magnesium, and calcium by precipitation with phenyl-thiohydantoic acid in slightly ammoniacal solution.

2. In the presence of iron the precipitate is rarely entirely free from this impurity, and usually contains from 1 to 5 mg., regardless of the amount originally present. This does not, however, interfere with the volumetric determination of cobalt.

3. Nickel is always partially precipitated.

4. The cobalt precipitate does not have a definite composition. It is probably contaminated with cobalt sulfide, thus making it necessary to convert the cobalt into some more definite form.

THE SEPARATION AND DETERMINATION OF COBALT. II. GRAVIMETRIC DETERMINATION OF COBALT

When determined gravimetrically cobalt is weighed as the oxide, Co_3O_4, as metal (obtained electrolytically or by reduction of the oxide in hydrogen), as sulfate, as double ammonium phosphate, or as pyrophosphate. Although other methods have been proposed they have proved unsatisfactory. The above methods were investigated in order to determine in what form cobalt could best be weighed after precipitation with phenyl-thiohydantoic acid.

Ignition to Oxide

Ignition to oxide is the method most commonly used when cobalt is precipitated by nitroso-β-naphthol or when it is obtained in any other suitable form.

To ascertain whether it is possible to ignite cobalt to a definite oxide, Co_3O_4, samples of the pure metal were dissolved in nitric acid and, after evaporation to dryness, ignited to constant weight in an electric furnace. Increase in the ignition temperature did not appreciably affect the results, as the following table indicates.

More satisfactory results were obtained by ignition in a porcelain crucible at the full heat of the Meker burner, possibly due to a slightly more reducing atmosphere. From the results given below it is evident that

TABLE I

EFFECT OF INCREASING IGNITION TEMPERATURE

Co taken	Co_3O_4 found at 850°	Co found	Co_3O_4 found at 900°	Co found
G.	G.	G.	G.	G.
0.0568	0.0779	0.0572	0.0782	0.0574
0.0429	0.0588	0.0432	0.0583	0.0428

upon ignition pure cobalt nitrate forms the oxide Co_3O_4, which may then be reduced in a stream of hydrogen to metal, so as to check with the theoretical value.

TABLE II

OXIDE IGNITED OVER MEKER BURNER THEN REDUCED IN HYDROGEN

Co taken	Co found as Co_3O_4	Co after ignition in hydrogen
G.	G.	G.
0.0842	0.0844	0.0844
0.0640	0.0639	0.0638
0.0646	0.0648	0.0648

Ignition to Oxide after Precipitation with Phenyl-thiohydantoic Acid

In order to determine whether cobalt could be ignited to oxide after precipitation by phenyl-thiohydantoic acid, samples of the pure metal were dissolved and precipitated by this reagent, as described in Paper I

TABLE III

IGNITION TO OXIDE

Co taken	Oxide found	Error assuming Co_2O_3	Error assuming Co_3O_4	Error, Co reduced in H
G.	G.	Mg. Co	Mg. Co	Mg.
0.0214	0.0354	+0.5	+1.7	...
0.0296	0.0432	+1.1	+2.3	...
0.0325	0.0463	+0.4	+1.5	...
0.0225	0.0326	+0.7	+1.4	...
0.0264	0.0386	+1.0	+2.2	...
0.0178	0.0252	+0.1	+0.7	...
0.0342	0.0472	−0.7	+0.4	...
0.0272	0.0388	+0.4	+1.3	...
0.0316	0.0446	+0.1	+1.2	...
0.0306	0.0431	0	+1.0	...
0.0327	0.0462	+0.1	+1.2	...
0.0171	0.0243	+0.2	+0.7	+0.9
0.0333	0.0456	−0.9	+0.1	−0.3
0.0278	0.0401	+0.6	+1.6	+1.7
0.0354	0.0504	+0.4	+1.6	+1.6
		Av. +0.3	Av. +1.3	Av. +1.0

(p. 7) and, after drying, ignited in porcelain crucibles to constant weight at the full heat of the Meker burner. In the preceding table it is evident that

more accurate results are obtained by assuming that the oxide is Co_2O_3 rather than Co_3O_4. In the last 8 experiments oxalic acid was added before ignition, and in the last 4 the oxide was reduced in hydrogen and the metal weighed.

In the following experiments every precaution was taken to make sure that none of the reagents gave non-volatile residues. Precipitation was made in a platinum dish to exclude silica from glass. Freshly distilled nitric acid and water were also used. Ammonium carbonate free from non-volatile matter was employed to make the solution ammoniacal. Phenyl-thiohydantoic acid recrystallized from water was used for the precipitation. These samples were ignited to oxide and then converted to sulfate after solution in perchloric acid. The results given here are excellent, assuming the oxide to be Co_2O_3.

TABLE IV

IGNITION TO OXIDE. FOLLOWED BY CONVERSION TO SULFATE

Co taken	Oxide found	Co calc. from Co_2O_3	Error	$CoSO_4$ found	Co calc. from sulfate	Error
G.	G.	G.	Mg.	G.	G.	Mg.
0.0272	0.0384	0.0273	+0.1	0.0709	0.0270	−0.2
0.0296	0.0518	0.0297	+0.1	0.0798	0.0303	+0.7
0.0404	0.0570	0.0405	+0.1	0.1054	0.0401	−0.3

Since it has been shown that the oxide formed on ignition corresponds to the formula Co_3O_4, the excess in weight must be due to some impurity or to the presence of cobalt in some form other than oxide. That this is not due to carbon, at least in any appreciable amount, was shown by the fact that the oxide was completely soluble in hydrochloric acid in the presence of a reducing agent. This solution of the oxide, however, gave a distinct test for sulfate.

It is evident, therefore, that during ignition some of the sulfur in the precipitate was converted into sulfate, thus causing the excess weight.

TABLE V

OXIDE CORRECTED FOR SULFATE

Co taken	SO_3 in ppt.	Corr. wt. of oxide	Co found	Error
G.	Mg.	G.	G.	Mg.
0.0566	1.6	0.0801	0.0576	+1.0
0.0404	1.3	0.0561	0.0402	−0.2
0.0308	1.2	0.0445	0.0318	+1.0
0.0329	0.7	0.0455	0.0329	0.0
0.0301	0.4	0.0412	0.0302	+0.1
0.0337	0.6	0.0467	0.0342	+0.5
0.0283	0.5	0.0386	0.0283	0.0
0.0334	0.5	0.0462	0.0339	+0.5
			Av.	+0.4

To detect the presence of sulfate, the cobalt oxide was dissolved in hydrochloric acid, evaporated to dryness, dissolved with water, diluted to 100

cc., the solution acidified with a few drops of hydrochloric acid and the sulfate precipitated as barium sulfate. The solutions were allowed to stand for 12 hours before filtration.

In all cases sulfate was found to be present, but this did not always account for the total excess weight. Possibly some of it was due to carbon, notwithstanding its seeming absence as stated above. The results are shown in Table V.

Electrolytic Determination of Cobalt

The electrolytic determination of cobalt is not always satisfactory. The deposit is often dark colored and contains impurity causing high results. Moreover, it is often impossible to obtain complete deposition. Lundell and Hoffman[15] have made a careful investigation of this matter and shown that excellent results may be obtained when the electrolyte contains a high concentration of ammonia and ammonium sulfate and a few grams of sodium sulfite. A few determinations were made under the conditions recommended and excellent results were indeed obtained. This method can, therefore, be considered satisfactory.

Determination as Cobalt Sulfate

In previous work in this laboratory it was shown that cobalt sulfate could be ignited at temperatures up to 550° without decomposition; above this there is a loss of sulfur trioxide. This temperature was, therefore, taken as most suitable for the ignition of the sulfate. Results are given in the preceding paper.[16]

Determination as Sulfate after Precipitation with Phenyl-thiohydantoic Acid

While it was possible to convert pure cobalt to the theoretical weight of sulfate, it was found that after precipitation with phenyl-thiohydantoic

Table VI

Determination As Sulfate

Co taken G.	$CoSO_4$ found G.	Co found G.	Error Mg.
0.0294	0.0780	0.0297	+0.3
0.0591	0.1541	0.0586	−0.5
0.0349	0.0929	0.0354	+0.5
0.0304	0.0803	0.0305	+0.1
0.0167	0.0489	0.0185	+1.8
0.0330	0.0877	0.0333	+0.3
0.0250	0.0666	0.0253	+0.3
0.0310	0.0814	0.0310	0.0
0.0343	0.0925	0.0352	+0.9
0.0522	0.1380	0.0525	+0.3
		Av.	+0.4

[15] Lundell and Hoffman, *J. Ind. Eng. Chem.*, **13**, 540 (1921).

[16] Table I, p. 7.

acid and conversion to sulfate, results were high. The cobalt sulfate never dissolved in water to give a solution entirely clear. A yellow precipitate separated which dissolved upon the addition of a drop of acid. The exact nature of this substance could not be determined because of the extremely small amount available. In the attempt to avoid this error, cobalt was precipitated according to the directions given in Part I and the precipitate treated in various ways.

1. After the carbon had been burned these samples were dissolved in hydrochloric acid, evaporated to dryness with sulfuric acid, ignited at 550°, and weighed as sulfate. The results are shown in Table VI.

2. If any of the excess weight were due to insoluble matter, filtering the solution and again evaporating to dryness should reduce the error. This process was used in 8 experiments. The insoluble portion was weighed and was found to contain about 0.1 mg. of iron and 0.1 mg. of cobalt. This does not account for the error in some of the results, and it would appear that part of the increased weight must be due to impurities which are soluble. The results obtained were even worse than the preceding, the average error being +1.0 mg., perhaps due to impurities derived from the glass vessels used in the second operation.

3. The dried precipitate was dissolved in perchloric acid, evaporated with sulfuric acid and weighed as cobalt sulfate. Care must be taken in dissolving the precipitate in perchloric acid, since the acid attacks organic matter quite vigorously. The cobalt sulfate did not dissolve in water to give a clear solution, but the results were more satisfactory.

Table VII

Determination of Sulfate After Solution in Perchloric Acid

Co taken G.	$CoSO_4$ found G.	Co found G.	Error Mg.
0.0235	0.0624	0.0237	+0.2
0.0257	0.0681	0.0259	+0.2
0.0137	0.0375	0.0143	+0.6
0.0325	0.0861	0.0327	+0.2

4. To make sure that no impurities were introduced by the reagents used, precipitation was made with the utmost care to exclude foreign substances, using specially purified materials, as described on p. 14. After conversion to sulfate, the results (Table IV, p. 14) show a slight error. The cobalt sulfate did not dissolve in water to give an entirely clear solution.

5. Ignition in a current of oxygen to oxide and then in a current of hydrogen to metal was tried, but it was impossible to obtain cobalt with a metallic luster. In 4 experiments the errors varied from +0.7 to +3.1 mg.

Determination of Cobalt as Pyrophosphate

The precipitation of cobalt as double ammonium phosphate has been

used by several investigators,[17] some of whom recognized that it gave rather erratic results. Precipitation is never complete and the cobalt in the filtrate must be recovered by precipitation as sulfide.

Fourteen experiments were made to test the accuracy of this method. The results were invariably too high, the error varying from 0.5 mg. to 4.2 mg. The filtrate and washings contained from 0.3 mg. to 2.9 mg. of cobalt. The method was as follows.

The cobalt solution was made neutral to litmus paper and 10 g. of diammonium hydrogen orthophosphate dissolved in 100 cc. of water was at first added drop by drop to the boiling solution, which contained 1 g. of ammonium chloride. The volume of the solution during precipitation was about 300 cc. Some solutions after cooling were filtered at once, some after standing for 2 hours and some after standing overnight. The character or solubility of the precipitate was not influenced by any of these modifications. The precipitate was filtered on a Gooch crucible, washed 20 times with a 1% solution of the ammonium phosphate, 10 times with cold water, and ignited at the full heat of the Meker burner to cobalt pyrophosphate, $Co_2P_2O_7$. The cobalt in the filtrate was precipitated as sulfide from an ammoniacal solution and ignited to oxide.

It is possible that the addition of less ammonium phosphate or some other change in the conditions of precipitation would have given better results; but the method must always be subject to the error due to solubility.

Summary

1. Although pure cobalt nitrate can be accurately ignited to the oxide, Co_3O_4, and the latter reduced by hydrogen to metal, the oxide obtained by ignition of the phenyl-thiohydantoic acid precipitate contains a little sulfate. If the oxide is empirically assumed to be Co_2O_3, the results are fairly good.

2. Ignition of cobalt sulfate at 550° is the most accurate method for cobalt. When applied to the phenyl-thiohydantoic acid precipitate the results are usually slightly high and the sulfate is not completely soluble in water.

3. The electrolytic determination of cobalt is very satisfactory when the proper conditions and precautions are observed.

4. Precipitation as cobalt ammonium phosphate followed by ignition to pyrophosphate is less accurate than the preceding methods.

[17] Dirvell, *Chem. News*, **40**, 268 (1880). Clarke, *ibid.*, **48**, 262 (1884). Hope, *J. Soc. Chem. Ind.*, **9**, 375 (1890). Dakin, *Z. anal. Chem.*, **39**, 784 (1900). Dufty, *J. Iron Steel Inst.*, **90**, 52 (1914).

THE SEPARATION AND DETERMINATION OF COBALT. III. THE VOLUMETRIC DETERMINATION OF COBALT

All of the volumetric methods for cobalt which have any claim to accuracy may be divided into two classes. In the first class the cobalt is oxidized to the trihydroxide by adding standard permanganate solution in the presence of a neutralizing agent, such as zinc oxide or mercuric oxide. The permanganate may be added in excess and the latter titrated with a suitable reducing agent.[18] The results obtained are only fairly good at best. In the second class the cobalt is oxidized to the trivalent form, (the trihydroxide, an amine or a compound with potassium hydrogen carbonate) by means of hydrogen peroxide,[19] hypochlorite,[20] bromine[21] or iodine.[22] After removing the excess of oxidizing agent, usually by filtering off the cobaltic hydroxide, the cobalt is reduced in acid solution to a cobaltous salt by means of standard ferrous sulfate or by potassium iodide, the iodine being titrated with thiosulfate solution. The composition of the oxide obtained by these different methods appears to vary considerably. Of the various oxidizing agents suggested, only iodine and hydrogen peroxide do not oxidize nickel; the excess of peroxide is easily removed by boiling, and an oxide of the theoretical composition is obtained without the necessity of a troublesome filtration; therefore, all other oxidizing agents were finally discarded by us. The use of hydrogen peroxide in a bicarbonate solution, as suggested by Job[19g], will be taken up later.

A few methods have been suggested, based upon the precipitation of cobalt as cyanide,[23] ferrocyanide,[24] or cobaltinitrite,[25] but these are very empirical and of comparatively little value. The alkalimetric titration of

[18] Winkler, *Z. anal. Chem.*, **3**, 265, 420 (1864). von Reis, *Z. angew. Chem.*, **3**, 695 (1890). Harris, *J. Am. Chem. Soc.*, **20**, 173 (1898).

[19] (a) McCulloch, *Chem. News*, **56**, 27 (1887). (b) Fischer, *Berg. Hüttenm. Ztg.*, **47**, 453 (1888). (c) Carnot, *Compt. rend.*, **108**, 610 (1889). (d) Moore, *Chem. News*, **82**, 73 (1900). (e) Metzl, *Z. anal. Chem.*, **53**, 537 (1914). (f) Engle and Gustavson, *J. Ind. Eng. Chem.*, **8**, 901 (1916). (g) Job, *Ann. chim. phys.*, **20**, 214 (1900).

[20] (a) Bayley, *Chem. News*, **39**, 81 (1879). (b) Fleischer, *J. prakt. Chem.*, **110**, 48 (1870).

[21] Ref. 19d. Taylor, *Chem. News*, **87**, 201 (1903).

[22] Donath, *Ber.*, **12**, 1868 (1879).

[23] McCulloch, *Chem. News*, **59**, 51 (1889). Rupp and Pfenning, *Chem.-Ztg.*, **34**, 322 (1910). Johnson, "Chemical Analysis of Special Steels," John Wiley and Sons, **1920**, 3d. Ed., p. 376.

[24] Jamieson, *J. Am. Chem. Soc.*, **32**, 757 (1910).

[25] Karlslake, *J. anal. Chem.*, **6**, 469 (1892).

cobalt-ammonium orthophosphate, $CoNH_4PO_4$, has also been suggested,[26] but this is subject to the errors mentioned in a previous paper (p. 16). Metzl[19e] was the first to give the details of a really accurate procedure involving the oxidation of cobalt to cobaltic hydroxide. He used two methods; in the first, hydrogen peroxide was added to a solution containing sodium bicarbonate and the green compound formed was decomposed by boiling with excess of sodium hydroxide, forming cobaltic hydroxide. In the second method, an ammoniacal solution of cobalt containing ammonium chloride was oxidized to a cobaltic amine by hydrogen peroxide. When this was boiled with excess of sodium hydroxide until all ammonia was expelled the amine was decomposed, forming cobaltic hydroxide. The first method is simpler and shorter. Nickel is not oxidized under these conditions. The excess of peroxide was destroyed by boiling, potassium iodide was added, the solution strongly acidified with sulfuric acid and when the precipitate had dissolved, the liberated iodine was titrated with thiosulfate solution. Excellent results were obtained in the presence of various amounts of nickel.

Engle and Gustavson[19f] used sodium perborate instead of hydrogen peroxide, and omitted the bicarbonate, adding directly an excess of sodium hydroxide. The excess of perborate was more readily destroyed than was peroxide, only 10 minutes' boiling being required. The subsequent operations were the same.

Oxidation to Cobaltic Hydroxide

Iodide as a Reducing Agent.—The method of Engle and Gustavson was first tried. The reaction is represented by the following equations.

$$8\,CoSO_4 + 4NaBO_3 + 14NaOH + 5H_2O = 8Co(OH)_3 + Na_2B_4O_7 + 8Na_2SO_4$$
$$2\,CO(OH)_3 + 2KI + 3H_2SO_4 = 2CoSO_4 + 2I + 6H_2O + K_2SO_4$$
$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Samples of metallic cobalt were dissolved in sulfuric acid, part of the latter was neutralized, 1 g. of sodium perborate was added, and then an excess of 3 g. of sodium hydroxide over that required to neutralize the solution. The solution in an Erlenmeyer flask was boiled for 10 minutes and cooled, carbon dioxide being passed through to expel the air. Two g. of potassium iodide was added, followed by 100 cc. of dil. sulfuric acid (1 of acid to 4 of water), making a total volume of 200 cc. The flask was stoppered and allowed to stand until the solution was clear, after which the iodine formed was titrated with 0.025 *N* thiosulfate solution standardized against pure potassium dichromate solution. The end-point was permanent in an atmosphere of carbon dioxide, even after standing for several hours.

A point not mentioned in previous work on this subject is the length of time required for the cobaltic hydroxide to dissolve, which varied from half an hour with small amounts to 2 hours with large amounts. This detracts considerably from the value of the method, since unless an atmos-

[26] Dakin, *Z. anal. Chem.*, **41**, 279 (1902). Schoeller and Powell, *Analyst*, **41**, 124 (1916); *J. Iron Steel Inst.*, **97**, 445 (1918).

phere free from oxygen is used this long exposure of the acid iodide solution causes the liberation of a slight excess of iodine.

A 10% stock solution of potassium iodide was prepared with water which had been boiled and cooled in an atmosphere of hydrogen. Blanks were run as follows.

A solution containing 200 cc. of water and 30 cc. of 10% sodium hydroxide was boiled for 10 minutes while carbon dioxide was passed through it and it was cooled; 20 cc. of potassium iodide solution was added, then 100 cc. of 1:3 sulfuric acid and the flask kept stoppered for 2 hours. The liberated iodine required 0.19–0.21 cc. of 0.025 *N* sodium thiosulfate solution, and accordingly a correction of 0.20 cc. was deducted in all titrations in which this solution was used. Later, another stock solution was prepared having a blank of 0.12 cc. It is possible that impurities in the sodium hydroxide may account for part of this blank.

In 30 determinations in which the weights of cobalt varied from 26 to 56 mg. the error varied from +0.2 to —0.8 mg., with an average of —0.2 mg.

Cobalt Determined After Precipitation with Phenyl-thiohydantoic Acid.—Samples of cobalt were dissolved in nitric acid, the solutions

TABLE I

COBALT AFTER PRECIPITATION WITH PHENYL-THIOHYDANTOIC ACID

Expt.	Co taken	0.025 *N* $Na_2S_2O_3$ Corrected	Co found	Error
	G.	Cc.	G.	Mg.
1	0.0201	13.73	0.0202	+0.1
2	0.0204	14.01	0.0206	+0.2
3	0.0310	21.12	0.0311	+0.1
4	0.0237	16.20	0.0240	+0.3
5	0.0215	14.68	0.0216	+0.1
6	0.0205	14.38	0.0201	−0.4
7	0.0294	20.14	0.0296	+0.2
8	0.0214	14.79	0.0218	+0.4
9	0.0248	17.03	0.0251	+0.3
10	0.0331	22.73	0.0335	+0.4
11	0.0262	17.87	0.0263	+0.1
12	0.0370	25.55	0.0376	+0.6
13	0.0278	19.05	0.0280	+0.2
14	0.0287	19.74	0.0290	+0.3
15	0.0255	17.34	0.0255	0
16	0.0356	24.26	0.0356	0
			Av.	+0.2

made ammoniacal, diluted to 200 cc., and the cobalt was precipitated with phenyl-thiohydantoic acid as previously described.[27] In the first 10 experiments the precipitate was removed from the filter paper and dissolved in 20 cc. of conc. hydrochloric acid and 50 cc. of conc. nitric acid. This had to be done carefully, as the oxidation of the carbonaceous matter

[27] p. 7.

was rather violent. The precipitate adhering to the filter paper was burned, dissolved in perchloric acid, and added to the main solution. Ten cc. of conc. sulfuric acid was added and, after evaporation of the solution to the appearance of fumes, sodium perborate was added and the determination carried out as previously described. In the last 6 experiments a more rapid and convenient procedure was adopted. The cobalt precipitate was dried and ignited to oxide. This oxide was then fused with potassium hydrogen sulfate and dissolved in water. A porcelain crucible was preferred to one of platinum, since, if the fusion was made in platinum, it was necessary to apply a blank correction for the amount of iron invariably extracted. In Expts. 15 and 16 a platinum crucible was used and a correction of 0.45 cc. of thiosulfate was applied. That the results are satisfactory is shown in Table I. The cobalt must be free from all metals which would be oxidized by hydrogen peroxide in alkaline solution and would thus affect the iodide titration. Attempts made to eliminate the oxidizing effect of iron upon the potassium iodide titration by the addition of fluoride or phosphate were unsuccessful. This metal must, therefore, be absent. The presence of nickel is entirely without effect.

Ferrous Sulfate as a Reducing Agent.—McCulloch[19a] and Fleischer[20b] used ferrous sulfate as a reducing agent, adding it to the strongly alkaline solution, acidifying and titrating the excess of ferrous iron with potassium permanganate or potassium dichromate solution. This method was tested by us but the results were always too low. After cooling, the cobaltic hydroxide solution was added to an excess of standard ferrous sulfate already acidified with 1:4 sulfuric acid. When ferrous sulfate is added to the alkaline solution, oxidation occurs and the results are too high. In most cases it required half an hour or longer to dissolve all the cobaltic hydroxide. The excess of ferrous sulfate was then titrated with permanganate or dichromate solution. With dichromate, ferricyanide was used as an external indicator; with permanganate, it was necessary to add nickel sulfate to eliminate the pink cobalt color; this is, however, unsatisfactory when more than 0.08 g. of cobalt is present.

The ferrous sulfate solution was standardized against the dichromate or permanganate solution. It was difficult to dissolve the last trace of cobaltic hydroxide. Heating facilitated solution, but in this case an atmosphere of carbon dioxide was required. If an empirical factor is employed, the results are quite satisfactory, as shown in Table II. The average factor calculated from Expts. 1–8 in which the excess was titrated with dichromate is 1.0475; from Expts. 9–13, in which permanganate was used, it is 1.0403. When these values are applied the error as shown in the last column becomes negligible in nearly every case. Although there is a loss of oxygen, indicating that ferrous sulfate is too weak a reducing

agent, this loss is remarkably constant and apparently varies directly with the amount of cobalt.

TABLE II

FERROUS SULFATE AS REDUCING AGENT

Expt.	Co taken G.	0.05 *N* $FeSO_4$ Cc.	Co found G.	Error Mg.	Error with empirical factor Mg.
1	0.0582	18.84	0.0555	−2.7	0
2	0.0462	14.96	0.0441	−2.1	0
3	0.0565	18.29	0.0539	−2.6	0
4	0.0481	15.57	0.0459	−2.2	0
5	0.0457	14.79	0.0436	−2.1	0
6	0.0435	14.08	0.0415	−2.0	0
7	0.0426	13.82	0.0407	−1.9	+0.1
8	0.0541	17.51	0.0516	−2.5	0
9	0.0853	27.79	0.0823	−3.0	−0.1
10	0 0530	17.28	0.0509	−2.1	0
11	0.0322	10.44	0.0308	−1.4	−0.2
12	0.0440	14.29	0.0421	−1.9	−0.2
13	0.0624	20.55	0.0606	−1.8	+0.6

One great advantage in the use of ferrous sulfate is that the presence of ferric iron does not interfere as it does with iodide, and as has been previously mentioned, traces of iron usually contaminate the cobalt when the latter is separated by phenyl-thiohydantoic acid. The reducing action of sodium arsenite, antimony trichloride, potassium thiocyanate and hydrazine salts was found to be very similar to that shown above, all the results being too low.

Stannous Chloride as a Reducing Agent.—Stannous chloride was found to be an admirable reducing agent. The reaction may be expressed by the following equation.

$$2Co(OH)_3 + SnCl_2 + 6HCl = 2CoCl_2 + SnCl_4 + 6\ H_2O.$$

The reduction is immediate and although any ferric iron present is reduced by the stannous chloride it is possible to titrate the excess of the latter by a reagent which also oxidizes the ferrous chloride formed. An atmosphere of carbon dioxide is absolutely necessary and the solution must be acidified as soon as an excess of the reducing agent has been added. The best results were obtained when the standard stannous chloride was made up with fairly concentrated hydrochloric acid so that every 30 cc. of stannous chloride contained 15 cc. of conc. hydrochloric acid. This left an excess of about 10 cc. of acid for each titration.

The excess of stannous chloride was titrated with several oxidizing agents. Iodine was found to be an excellent one on account of the sharpness of the end-point, but it had the disadvantage of requiring a special procedure when iron was present, unless a correction was applied for the

amount of iron reduced, which is usually unknown. Potassium bromate, potassium iodate and potassium dichromate all gave satisfactory results and will be separately discussed.

Titration of Excess of Stannous Chloride by Iodine.—Cobalt was oxidized in alkaline solution, as previously described, in a 500cc. flask provided with a side tube extending to the bottom. The total volume was kept at about 150 cc. After boiling to remove the excess of oxidizing agent the solution was cooled while carbon dioxide was passed through it, and the strongly acid standard solution of stannous chloride added. The solution cleared *immediately*, giving a pink solution of cobalt chloride. The excess of stannous chloride was then determined with standard iodine, potassium bromate or iodate, potassium iodide being added in the latter cases so that the usual iodine end-point was obtained. The results are shown in Table III. The average error is 0 mg.

TABLE III

REDUCTION BY STANNOUS CHLORIDE AND TITRATION OF EXCESS IODIMETRICALLY

Co taken G.	0.1 *N* $SnCl_2$ added Cc.	0.1 *N* iodine Cc.	Co found G.	Error Mg.
0.0812	23.50	9.69	0.0813	+0.1
0.0686	22.10	10.47	0.0686	0
0.0842	24.31	10.02	0.0842	0
0.0662	21.97	10.74	0.0662	0
0.0575	21.24	11.45	0.0576	+0.1
0.0457	19.47	11.76	0.0455	−0.2
0.0694	23.58	11.83	0.0694	0
0.0704	23.49	11.45	0.0709	+0.5
0.0512	20.41	11.73	0.0512	0
0.0576	21.88	12.05	0.0576	0
0.1323	33.74	11.43	0.1316	−0.7
0.0883	25.93	10.96	0.0883	0
		$KBrO_3$		
0.0757	23.42	10.67	0.0752	−0.5
0.0860	24.27	9.70	0.0860	0
0.0701	21.50	9.50	0.0706	+0.5
		KIO_3		
0.0819	19.02	5.20	0.0815	−0.4
0.0595	19.39	9.32	0.0594	−0.1
0.0458	15.39	7.55	0.0462	+0.4

In this process, the presence of iron would introduce an error, as it is not re-oxidized by these reagents.

Titration of Excess of Stannous Chloride by Potassium Dichromate.—When the excess of stannous chloride is oxidized by potassium dichromate solution, the iron which has been reduced by the tin will be oxidized by the dichromate and no error will be introduced. In this method, the cobalt solution was oxidized in the manner described above, and after reduction

by stannous chloride, an excess of potassium dichromate solution was added. The current of carbon dioxide was then discontinued and the solution was transferred for convenience to a beaker, 30 cc. of 5 *N* ferric chloride solution was added to increase the delicacy of the end-point and the excess of dichromate was titrated with standard ferrous sulfate; ferri-

TABLE IV

EFFECT OF IRON ON OXIDATION OF COBALT

Co taken	Fe added	0.05 *N* $SnCl_2$	0.05 *N* $K_2Cr_2O_7$	Co found	Error
G.	Mg.	Cc.	Cc.	G.	Mg.
0.0529	10.0	31.85	14.19	0.0520	−0.9
0.0522	10.0	31.85	14.38	0.0515	−0.7
0.0442	10.0	31.08	16.11	0.0441	−0.1
0.0319	10.0	25.48	15.01	0.0309	−1.0
0.0660	7.0	38.22	15.86	0.0659	−0.1
0.0542	7.0	31.85	13.42	0.0543	+0.1
0.0405	7.0	25.48	11.70	0.0406	+0.1
0.0640	7.0	31.87	10.16	0.0640	0
0.0394	7.0	25.48	12.20	0.0391	−0.3
0.0469	7.0	25.54	9.51	0.0472	+0.3
0.0450	7.0	25.60	10.45	0.0447	−0.3
0.0471	5.0	38.22	22.29	0.0470	−0.1
0.0405	5.0	31.85	18.18	0.0403	−0.2
0.0437	5.0	31.85	16.81	0.0443	+0.6
0.0515	5.0	31.85	14.38	0.0515	0
0.0439	5.0	25.48	10.61	0.0439	0
0.0352	0.0	28.80	16.85	0.0352	0
0.0252	0.0	28.65	20.08	0.0252	0
0.0227	0.0	28.65	20.98	0.0226	−0.1
0.0318	0.0	28.98	18.21	0.0317	−0.1

cyanide was the external indicator. The concentration of hydrochloric acid should not be increased, because this decreases the delicacy of the end-point. If the excess of dichromate should be titrated electrometri-

TABLE V

COBALT FIRST PRECIPITATED BY PHENYL-THIOHYDANTOIC ACID IN PRESENCE OF 1 G. OF IRON

Co taken	0.05 *N* $SnCl_2$	0.05 *N* $K_2Cr_2O_7$	Co found	Error
G.	Cc.	Cc.	G.	Mg.
0.0251	24.92	16.27	0.0252	+0.1
0.0286	28.65	18.94	0.0286	0
0.0334	28.65	17.39	0.0332	−0.2
0.0264	28.80	19.92	0.0262	−0.2
0.0227	28.65	21.04	0.0224	−0.3
0.0236	28.98	21.04	0.0234	−0.2
0.0260	29.04	20.42	0.0254	−0.6
0.0232	30.01	22.36	0.0228	−0.4

cally this would become the most rapid and accurate of all volumetric methods for cobalt. The iron was added in the form of ferric alum before the oxidation of the cobalt, and its effect in the latter process is shown in Table IV.

It is evident that the presence of 10 mg. of iron causes incomplete oxidation of the cobalt, while 7 mg. has no effect.

Pure cobalt solutions were precipitated by phenyl-thiohydantoic acid in the presence of 1 g. of iron. The precipitate was dried, fused with potassium bisulfate, dissolved in water, oxidized, dissolved in stannous chloride and the excess titrated as above. A single precipitation of cobalt under favorable conditions will carry less than 7 or 8 mg. of iron, so that no error is introduced, as is shown in Table V.

Effect of Presence of Copper.—Copper is often associated with cobalt, and unless this element has previously been removed it will precipitate quantitatively with the cobalt upon the addition of phenyl-thiohydantoic acid. Experiments were performed to see what effect copper might have on the oxidation of the cobalt in alkaline solution. Copper does not seem to interfere with the oxidation of the cobalt, but when 13 mg. is present the end-point with potassium ferricyanide is difficult to detect, since copper reacts with the indicator. This is evident from the results in Table VI.

TABLE VI

EFFECT OF COPPER ON OXIDATION OF COBALT

Co taken	Cu added	0.05 *N* $SnCl_2$	0.05 *N* $K_2Cr_2O_7$	Co found	Error
G.	Mg.	Cc.	Cc.	G.	Mg.
0.0214	5.5	28.95	21.67	0.0214	0.0
0.0250	5.5	28.95	20.34	0.0253	+0.3
0.0257	6.07	28.95	20.19	0.0258	+0.1
0.0235	6.25	24.10	16.07	0.0237	+0.2
0.0208	9.2	24.10	17.07	0.0207	−0.1
0.0254	10.02	24.10	15.34	0.0258	+0.4
0.0258	13	24.10	15.16	0.0263	+0.5
0.0321	13.12	24.10	13.03	0.0326	+0.5

Separation of Iron from Cobalt by means of Zinc Oxide.—The separation of iron from cobalt by precipitation of the former as ferric hydroxide by means of zinc oxide was tested, as it is recommended by certain steel chemists.[28] The solution, which contained 1 g. of iron, was diluted to a definite volume, allowed to settle, aliquot portions were taken and the cobalt was titrated as above. No account was taken of the volume occupied by the precipitate. The results were invariably several milligrams too low.

Oxidation of Both Stannous and Ferrous Chlorides by Iodine in Neutral Solution.—When cobalt is oxidized in the presence of a little iron, iodine may be used in acid solution to titrate the excess of stannous chloride if a correction is applied for the ferrous chloride formed as previously mentioned (p. 23), but in a neutral solution in the presence of pyrophosphate the ferrous iron also is oxidized. The latter reaction becomes very slow towards the end, and it is, therefore, necessary to add

[28] Scott, "Standard Methods of Analysis," D. Van Nostrand & Co., 1920, p. 148.

excess of iodine and titrate back with thiosulfate solution. On account of the sharpness of the iodine end-point this method is a desirable one.

The concentration of hydrogen ion must be sufficient to prevent any reaction between iodine and hydroxyl ion (P_H not over 7.5) and not too great to allow complete reaction with ferrous iron. A solution neutral to aurine (4,4′-dihydroxy-diphenyl-quinomethane), (P_H about 6.6) or barely acid to bromothymol-sulfonephthalein was satisfactory for this purpose.

The cobalt, with 5 mg. of iron, was oxidized with perborate in sodium hydroxide solution and reduced by excess of stannous chloride as previously described. This excess was removed by the addition of standard iodine and the slight excess of iodine removed by a drop of thiosulfate solution, the ferrous chloride not being oxidized. Aurine was added, then 5 g. of sodium pyrophosphate crystals and sufficient sodium bicarbonate to change the yellow of the indicator to orange. Iodine in excess was then added and the excess titrated with thiosulfate. This last amount of iodine reacts with the iron reduced by the stannous chloride. The stannous chloride was standardized against the iodine solution and the results were the same whether the acid solution was titrated directly with iodine or whether the stannous salt was added to an alkaline solution containing iron and the above procedure followed.

TABLE VII

EXCESS OF STANNOUS CHLORIDE IN PRESENCE OF IRON TITRATED IODIMETRICALLY IN NEUTRAL SOLUTION

	Co taken G.	0.05 *N* $SnCl_2$ Cc.	0.05 *N* Iodine Cc.	Co found G.	Error Mg.
1	0.0475	28.35	12.30	0.0473	−0.2
2	0.0451	28.35	13.06	0.0451	0
3	0.0575	28.08	8.50	0.0577	+0.2
4	0.0578	28.08	8.35	0.0581	+0.3
5	0.0430	28.08	13.44	0.0432	+0.2
6	0.0510	28.08	10.74	0.0511	+0.1
7	0.0340	28.08	16.48	0.0342	+0.2
8	0.0308	28.08	17.47	0.0312	+0.4
9	0.0329	27.96	16.84	0.0328	−0.1
10	0.0315	27.96	17.30	0.0315	0
11	0.0425	27.96	13.54	0.0425	0

Since the color change of aurine is influenced somewhat by the pink color of the cobalt and since bromothymol-sulfonephthalein is not blue at this point it seemed desirable to simplify this part of the process by neutralizing the solution after the titration of the excess of stannous chloride. Tetrabromo-phenolsulfonephthalein was used as indicator, since its change to blue is not obscured by the color of the cobalt. If now, 1 to 2 g. of sodium bicarbonate is added, the solution, 150 cc. in volume, will be neutral to aurine and ready for the iodine titration.

The stannous chloride was standardized against the iodine solution under the same conditions. Table VII shows the results obtained. Five mg. of iron was present in all cases. In Expts. 1–8 the solutions were neutralized by the first method, and in 9–11 by the second.

Stannous Sulfate as a Reducing Agent.—If the excess of reducing agent could be titrated with potassium permanganate solution, the process would be much simplified, but sulfate solutions would then be necessary. A solution of stannous sulfate containing 150 cc. of sulfuric acid per liter was made up and standardized against potassium permanganate solution. The stannous sulfate was added to the alkaline solution just as was done with stannous chloride. Results show that it is a much weaker reducing agent than the chloride and, like ferrous sulfate, not powerful enough to retain all the oxygen, the error with 80 mg. of cobalt varying from —1.4 to —2.7 mg.

Stannous pyrophosphate in neutral solution was useless as the cobalt precipitate did not dissolve even after long standing unless the solution was strongly acidified.

Titanous Sulfate as a Reducing Agent.—The salts of trivalent titanium are even more powerful reducing agents than stannous chloride and when sulfate solutions are used the excess may be titrated with potassium permanganate, thus eliminating the effect of iron. The reduction of cobaltic hydroxide may be expressed by the following equation.

$$Ti_2(SO_4)_3 + 2Co(OH)_3 + 3H_2SO_4 = 2\ Ti(SO_4)_2 + 2CoSO_4 + 6H_2O.$$

In alkaline solution the reaction, $2Ti(OH)_3 + 2H_2O = 2Ti(OH)_4 + H_2$, occurs, and it is essential that the titanous sulfate be added to a solution which is not strongly alkaline, or that the latter be promptly acidified by the simultaneous addition of acid. To accomplish this purpose 4 methods were used, the cobalt having previously been oxidized in the usual way by perborate in a solution containing 3 g. of sodium hydroxide in a volume of about 100 cc. (1) The solution was partly neutralized by passing into it for 15 minutes a rapid current of carbon dioxide; (2) 12 g. of boric acid was added, which is 80% of the amount required to give a solution neutral to phenolphthalein; 10 g. was too little, 15 g. too much; (3) half the amount of monopotassium orthophosphate required to form a dibasic phosphate was added, but as this had to be followed by a current of carbon dioxide for 15 minutes it offers no advantage over (1) or (2) and is not recommended because it forms a precipitate of titanic phosphate. (4) dil. sulfuric acid was added simultaneously with the titanous sulfate. This gives good results when the acid is added at the proper rate, but on account of the care needed in this operation the method is not recommended.

The titanous sulfate was prepared by the electrolytic reduction of titanic sulfate. An approximately 0.05 *N* solution was prepared, containing 150 cc. of conc. sulfuric acid per liter. It was stored under a slight pressure of carbon dioxide with no unusual precautions to avoid leakage. The solution oxidized slowly and rather irregularly.

Just before using, it was standardized against permanganate which, in turn, had been standardizied against sodium oxalate. Whether it was titrated directly against permanganate or added to an alkaline solution previously boiled and cooled in carbon dioxide, the alkali being neutralized by the acid in the standard solution, made no difference. The lavender-colored solution became colorless just before the end-point was reached. It was observed that when the titanous salt was added to a solution sufficiently alkaline to cause slight oxidation, the color of the solution when acidified was a deep amethyst instead of the usual light lavender. All titrations were conducted in an atmosphere of carbon dioxide.

The results are shown in Table VIII. In Expts. 1–6, Method 1 was used; in 7–10, Method 2; in 11–15, Method 3; and in 16–19, Method 4. Samples of pure cobalt were used in all cases. Experiments in which the cobalt was first precipitated by phenyl-thiohydantoic acid in the presence of 1 g. of iron, and in which Method 4 was used were given in Table II, of Paper I.[29]

TABLE VIII

REDUCED BY TITANOUS SULFATE

	Co taken	0.05 *N* $Ti_2(SO_4)_3$ added	0.05 *N* $KMnO_4$	Co found	Error
	G.	Cc.	Cc.	G.	Mg.
1	0.0724	35.52	11.05	0.0721	+0.3
2	0.0738	35.52	10.45	0.0739	+0.1
3	0.0575	35.06	15.64	0.0573	−0.2
4	0.0555	35.07	16.18	0.0553	−0.2
5	0.0731	35.07	10.35	0.0730	−0.1
6	0.0522	35.07	17.37	0.0522	0
7	0.0309	20.16	9.61	0.0311	+0.2
8	0 0417	25.20	11.07	0.0417	0
9	0.0653	30.24	8.17	0.0651	−0.2
10	0.0229	20.16	12.50	0.0226	−0.3
11	0.0370	21.02	8.33	0.0366	−0.4
12	0.0205	15.60	8.63	0.0205	0
13	0.0282	10.81	11.24	0.0282	0
14	0.0655	31.21	8.80	0.0661	+0.4
15	0.0385	25.75	12.66	0.0385	0
16	0.0309	22.34	11.86	0.0309	0
17	0.0314	21.66	10.87	0.0319	+0.4
18	0.0335	22.34	10.94	0.0336	+0.1
19	0.0289	20.10	10.33	0.0288	−0.1

Conclusions.—The oxidation to cobaltic hydroxide by perborate in alkaline solution is incomplete when more than 7 mg. of iron is present.

Cobaltic hydroxide may be quantitatively reduced and determined volumetrically by the following methods: (1) by potassium iodide in acid solution, but the reaction is slow and iron must be absent; (2) by an acid ferrous sulfate solution, the excess of which is titrated with permanganate; an empirical factor must be used in this case; (3) by a

[29] p. 9

strongly acid solution of stannous chloride, the excess of which is titrated with iodine, iodate, bromate or dichromate; if iron is present iodine will oxidize it quantitatively only in a neutral solution; (4) by acid titanous sulfate added to the neutralized solution, the excess of which, together with any ferrous salt formed, is titrated with permanganate.

Oxidation of Cobalt in Potassium Hydrogen Carbonate Solution

Job[19g] suggested a volumetric determination of cobalt based upon its oxidation by hydrogen peroxide in potassium bicarbonate solution to a green, trivalent compound to which he assigned the formula, K_3CoO_3. This was reduced by excess of standard ferrous pyrophosphate and the excess was titrated with permanganate. He gave few results and meager details. According to Durrant[30] the cobalt compound has the structural formula $(KCO_2-O)_2>CO-O-CO<(OCO_2K)_2$ and the reaction proceeds according to the equation, $4KHCO_3 + 2CoCO_3 + H_2O_2 = (Co(KCO_3)_2)_2 O + 2CO_2 + 2H_2O$. The compound is stable only in the presence of a high concentration of bicarbonate, for which reason only potassium bicarbonate can be used. When heated it forms cobaltic hydroxide. The excess of peroxide seems to decompose very quickly even at room temperature, but the dissolved oxygen with perhaps traces of peroxide must be removed by passing carbon dioxide through the warm solution. This is the critical part of the method, for when the solution is too warm or the time too protracted, some decomposition occurs while, on the other hand, there is danger of not removing all of the excess of oxygen. The limits here are rather narrow and affected to some extent by the presence of other metals. It was necessary, therefore, to study carefully the effects of varying these conditions.

The following procedure was adopted.

To the slightly acid solution of cobalt 10 cc. of 3% hydrogen peroxide was added and potassium bicarbonate until a green color appeared, then 30 g. in excess. The precipitate which formed dissolved in the excess. The solution, 150 cc. in volume, was heated to the temperature stated in the table and a rapid current of carbon dioxide was passed through it. It was cooled quickly, 5 g. of powdered crystallized sodium pyrophosphate was added and then ferrous sulfate until a deep pink color appeared, showing reduction to cobaltous pyrophosphate. Twenty-five cc. of 1:1 sulfuric acid was added to neutralize the bicarbonate, with great care on account of the violence of the effervescence, after which the current of gas was discontinued. The excess of ferrous sulfate was then titrated with permanganate solution. The pink color of the cobalt was eliminated by adding nickel sulfate; 1 or 2 cc. of 0.05 *N* ferrous sulfate solution was added in excess; 1 cc. of 0.05 *N* solution is equivalent to 2.948 mg. of cobalt.

The effect of varying the temperature and time of heating is shown in Table IX. The weight of cobalt in each experiment varied between 38 and 65 mg.

[30] Durrant, *J. Chem. Soc.*, **87**, 1781 (1905).

Discrepancies will be observed in this table, for the method does not give quite as concordant results as does oxidation to cobaltic hydroxide; heating for 5 minutes at 63°, however, seems to be quite satisfactory.

TABLE IX

EFFECT OF TEMPERATURE AND TIME OF HEATING

Temperature ° C.	Time of heating Min.	Error Mg.	Temperature ° C.	Time of heating Min.	Error Mg.
85	20	−1.3	63	5	+0.1
85	10	−0.2	63	3	−0.3
65	10	−0.8	63	1	−0.3
63	15	−0.4	60	30	0
63	5	0	60	0	+1.2
63	5	+0.3	50	5	+0.3
63	5	−0.2	43	5	+1.2
63	5	−0.1	20	10	+1.5
63	5	+0.2	20	12 hrs.	+0.7

The advantage of this method lies in the fact that the interference of moderate amounts of arsenic, iron and manganese, is less than in the

TABLE X

EFFECT OF OTHER METALS

	Co taken G.	Fe added G.	As added G.	Ni added G.	Mn added G.	Co found G.	Error Mg.
1[a]	0.0440	0.012	...	...	...	0.0437	−0.3
2[a]	0.0772	0.033	...	...	...	0.0766	−0.6
3	0.0410	0.055	...	...	...	0.0397	−1.3
4	0.0491	0.055	...	...	...	0.0468	−0.3
5	0.0540	0.088	...	...	...	0.0536	−0.4
6	0.0736	0.099[b]	...	...	...	0.0731	−0.5
7	0.0430	...	0.140	...	...	0.0431	+0.1
8	0.0607	...	...	0.030	...	0.0604	−0.3
9	0.0643	...	...	0.100	...	0.0639	−0.4
10	0.0439	...	...	0.200	...	0.0437	−0.2
11	0.0540	...	...	0.250	...	0.0513	−2.7
12	0.0575	0.005	...	0.250	...	0.0575	0
13	0.0711	0.088	...	0.250	...	0.0710	−0.1
14	0.0531	...	0.350	0.250	...	0.0331	−20.0
15	0.0471	0.055	0.140	0.250	...	0.0444	−2.7
16	0.0659	0.023	0.350	0.100	...	0.0599	−6.0
17	0.0470	0.012	0.140	0.040	...	0.0455	−1.2
18	0.0543	...	...	...	0.012	0.0513	−3.0
19	0.0458	0.055	...	...	0.025	0.0456	−0.2
20	0.0370	0.005	...	...	0.006	0.0385	+1.5
21	0.0795	0.077	...	...	0.006	0.0796	+0.1

[a] Heated to 63° for 5 minutes.

[b] 50 g. of $KHCO_3$ added.

other, as shown in Table X. The effect of large amounts of iron is to decrease the maximum temperature permissible in destroying the excess of

peroxide. The arsenic was added as arsenic acid, the other metals as sulfates. Thirty g. of potassium bicarbonate was added except when 99 mg. of iron was present, when it was increased to 50 g. All solutions were heated to 50° for 5 minutes unless otherwise noted. The results are shown in the preceding table. The effect of iron is much less with this method than in strongly alkaline solution. It is necessary to add sufficient bicarbonate to obtain a clear solution, which, if 0.1 g. of iron is present means about 50 g. Nickel, even in small amounts will not dissolve in excess of bicarbonate; when a little iron is also present, however, a clear solution is obtained unless the amount of nickel is very large. It is, therefore, desirable to add about 5 mg. of iron if none is present (Expts. 11 and 12); 250 mg. of nickel alone always gave low results; less than that did not introduce much of an error. It was thought that possibly the presence of the nickel precipitate caused a slight decomposition of the cobalt compound and the attempt was made to avoid this by adding pyrophosphate before or after the oxidation, but no appreciable improvement resulted. Manganese is not oxidized by peroxide in bicarbonate solution but, like nickel, is insoluble in excess of bicarbonate. Even 6 mg. caused low results. In the presence of sufficient iron, however, a clear solution resulted if not over 25 mg. was present, and accurate results were obtained. More iron is required than in the case of nickel (Expts. 18–21). Arsenic alone is without effect, but in the presence of nickel the results are very low and even when iron is added the error is serious (Expts. 7, 14–17).

Iodine may be used to titrate the excess of ferrous pyrophosphate as described in the preceding method (p. 26) if the bicarbonate is partly neutralized. A solution of 30 g. of potassium bicarbonate and 5 g. of sodium pyrophosphate in a volume of 150 cc. was neutralized with 1:1 sulfuric acid until aurine added as indicator became orange; 12–15 cc. of acid gave satisfactory results, while with 17 cc. the oxidation of iron was incomplete.

A few other experiments on the titration of ferrous pyrophosphate with iodine will be recorded here because of their possible value in other reactions in which this reducing agent is used. To 30 cc. of 0.05 *N* ferrous sulfate solution were added 10 cc. of hydrochloric acid (sp. gr. 1.18), 100 cc. of water, 5 g. of sodium pyrophosphate decahydrate and various amounts of sodium bicarbonate. Oxygen was excluded by a current of carbon dioxide. A slight excess of standard iodine solution was added, the gas current stopped and the excess of iodine titrated with standard thiosulfate solution. With 8 g. of bicarbonate the error was —0.06 cc. of 0.05 *N* iodine, with 10 g., +0.06 cc. (average of 11 titrations); with 12 g., —0.04 cc., and with 15 g., +0.33 cc. It is evident that the amount of sodium bicarbonate can vary between 8 and 12 g. A similar set of

experiments was run using borax and boric acid instead of bicarbonate, except that only 5 cc. of hydrochloric acid was added. The results are shown in Table XI.

TABLE XI

TITRATION OF FERROUS PYROPHOSPHATE WITH IODINE

			No boric acid	
Borax added	Boric acid added	Error 0.05 *N* iodine	Borax added	Error 0.1 *N* iodine
G.	G.	Cc.	G.	Cc.
20	0	−3.28	15	−0.74
40	0	−0.20	25	−0.84
45	0	−0.04	30	−0.37
50	0	−0.06	35	−0.12
30	2	−0.03	40	−0.08
30	5	−0.16	45	+0.03
30	10	−0.49	50	+0.30

About 45 g. of borax is the proper amount. On account of the quickness with which it dissolves, bicarbonate is somewhat more satisfactory.

Conclusions.—Although cobalt is completely oxidized by hydrogen peroxide in bicarbonate solution the compound is not very stable and care must be used in removing the excess of peroxide before reduction with ferrous pyrophosphate.

Moderate amounts of iron, nickel and arsenic do not interfere when present separately, but low results are obtained when all three or the two latter are present. Manganese is not oxidized and in small amounts does not interfere if sufficient iron is present. In general, the presence of a small amount of iron is desirable.

Determination of Cobalt in Steel

The methods described in this paper were applied to the determination of cobalt in alloy steels. Samples weighing 0.7 g. were treated with 40 cc. of hydrochloric acid (sp. gr. 1.1). The tungsten separated as a black powder. One or 2 cc. of 85% phosphoric acid and 3 cc. of nitric acid were added slowly and the solution was kept hot until everything was dissolved. Seven g. of citric acid was added, then conc. ammonia until the solution was alkaline and finally 6 cc. in excess. To the hot alkaline solution was added with constant stirring 1 g. of phenyl-thiohydantoic acid dissolved in 30 cc. of hot water. The cobalt precipitated at once, and the solution was boiled for a few minutes with vigorous stirring to prevent bumping. It required longer than usual to obtain complete precipitation, and this was facilitated by agitating the solution. In all cases, the filtrates were found to be free from cobalt. The precipitate was dried, ignited, fused with potassium pyrosulfate and dissolved in water. In Sample A the cobalt was oxidized with perborate and reduced with stannous chloride, the excess of which was titrated with dichromate. In Sample B (British

Standard Cr V W Co. Steel "W") the cobalt was oxidized in bicarbonate solution and reduced with ferrous pyrophosphate, the excess of which was titrated with permanganate solution. Sample A was precipitated twice, although this was not necessary. The results are given in Table XII.

TABLE XII

DETERMINATION OF COBALT IN ALLOY STEELS

	Co found %	Co present %
Cr V W Co. Steel A	3.77 3.75 3.74 3.75	3.84[a]
Cr V W Co. Steel B	4.88 4.91	4.76[b]

[a] Value obtained by works chemist who precipitated cobalt with nitroso-β-naphthol after removal of tungsten and iron and weighed as Co_3O_4.

[b] Certificate value. Results of individual analysts varied from 4.53 to 4.99.

Summary

1. For the determination of cobalt, volumetric methods are in general the most accurate and satisfactory.

2. The most accurate method involves the oxidation of cobalt to cobaltic hydroxide in strongly alkaline solution by means of perborate or hydrogen peroxide, followed by its volumetric reduction to a cobaltous salt. This reduction may be accomplished by the following methods.

(a) By potassium iodide in acid solution, the iodine liberated being titrated with thiosulfate; iron must be absent.

(b) By adding the cobaltic hydroxide to an acid ferrous sulfate solution, the excess of which is titrated with permanganate solution. An empirical factor must be used.

(c) By a strongly acid solution of stannous chloride, the excess of which is titrated with iodine, iodate, bromate or dichromate solution. The last, titrated electrometrically, is especially recommended. If iron is present, iodine will oxidize it quantitatively only in a neutral solution.

(d) By titanous sulfate, the excess of which is titrated with permanganate. Since titanous hydroxide decomposes water with liberation of hydrogen, the alkaline solution must first be almost completely neutralized by one of several methods suggested.

3. Nickel does not interfere, but the oxidation is incomplete when more than 7 mg. of iron is present.

4. In the presence of a large excess of potassium bicarbonate, cobalt is oxidized by hydrogen peroxide to a green, trivalent compound, which is reduced in the presence of pyrophosphate by ferrous sulfate, the excess of which is titrated with permanganate after acidifying with sulfuric acid.

5. Iron and manganese in small amounts do not interfere in this method,

but the principal source of error is in the removal of excess peroxide without decomposing the cobalt compound.

6. Cobalt in alloy steels was determined volumetrically after separation by phenyl- thiohydantoic acid.

COLORIMETRIC DETERMINATION OF COBALT

For the colorimetric determination of cobalt several method have been proposed. The intense blue color of cobalt salts in concentrated hydrochloric acid solution was employed by Huttner[31] and the blue color of cobalt ammonium thiocyanate was suggested by Powell[32]. Jones[33] made use of the color developed by α-nitroso-β-naphthol in citrate solution. It was thought that the green color formed when cobalt is oxidized by hydrogen peroxide in bicarbonate solution might be intense enough to be used in colorimetric work. This compound has already been described in connection with the volumetric determination of cobalt. Oxalate, succinate, citrate and tartarate solutions also give similar compounds, varying in color from brown to green, but they were found to be either less intense or less stable than the bicarbonate compound.

It was found that 1.0 mg. of cobalt in 100 cc. is the minimum concentration which can be used in colorimetric comparisons. Solutions containing from 1 mg. to 3 mg. in 100 cc. were compared in a Kober colorimeter. The error varied from —0.15 mg. to +0.3 mg. The method may therefore be considered fairly accurate when the amount of cobalt present is not too small. The attempt was made to form a colloidal solution of the precipitate formed by phenyl-thiohydantoic acid, using a protective colloid. Comparatively little color was obtained, however.

THE SEPARATION OF COPPER BY MEANS OF PHENYL-THIOHYDANTOIC ACID

During the course of an investigation on the separation of cobalt by means of phenyl-thiohydantoic acid[34] it was found that in a solution slightly acid with acetic acid, copper, lead, mercury, cadmium, bismuth and antimony are quantitatively precipitated by this reagent, while tin, arsenic and the metals not in the hydrogen sulfide group are not precipitated under these conditions. The bismuth and antimony compounds are soluble in alcohol. The present paper gives the details of the separation of copper by this means.

When pure, the precipitate is bright yellow, but it decomposes so readily to form sulfide that it is usually a dirty yellow. It is, therefore, impossible

[31] Huttner, *Z. Anorg. allgem. Chem.*, **86,** 341(1914)

[32] Powell, *J. Soc. Chem. Ind.*, **36,** 273 (1917).

[33] Jones, *Analyst*, **43,** 317 (1918)

[34] p. 5.

to weigh the copper in this form. When ignited to oxide, the latter contained sufficient sulfate to cause an error varying from +0.1 to +0.6 mg. It was found desirable, therefore, to dissolve this oxide, preferably by fusion with potassium pyrosulfate, and to determine the copper by any of the well-known methods.

Procedure

The solution is neutralized with ammonia and 5 cc. of glacial acetic acid added. If metals precipitated by ammonia are present, 7 g. of citric acid is first added for every gram of metal. To the boiling solution, 300–400 cc. in volume, is added 0.5 g. of phenyl-thiohydantoic acid dissolved in a little hot water, then dil. ammonium hydroxide until a yellow precipitate just begins to form. It is well at this point to discontinue the addition of ammonia and to boil the solution for a few minutes. If the copper is all precipitated, the yellow precipitate separates at the top leaving a clear solution. If this does not occur, more aqueous ammonia should be added; too much causes appreciable solubility of the precipitate. It also turns brown from the formation of sulfide. Precipitation is complete at once. The solution is filtered hot and the precipitate washed with hot water. It is ignited to oxide, fused with potassium pyrosulfate, dissolved in water and the copper determined electrolytically or volumetrically. If preferred, the oxide may be dissolved in hydrochloric acid. This separation is best adapted for amounts of copper less than 0.1 g.

As in the case of cobalt, the separation from iron was found to be the most difficult; consequently this is the only one which was studied in detail. In the other cases it was simply shown that the copper was completely precipitated and that no trace of other metals was carried down. If the amount of reagent was doubled a much greater amount of iron was carried down. Samples of an imported pure electrolytic copper were weighed out and dissolved in nitric acid; 1 g. of iron was added as ferric alum, and the copper precipitated as described above, after which it was determined electrolytically. The results are shown in the following table. In Expts. 1–5, 1 g. of reagent was added; in the others, 0.5 g.

Expt.	Cu taken G.	Cu found G.	Error Mg.	Fe in ppt. Mg.
1	0.1051	0.1050	−0.1	8.4
2	0.0676	0.0676	0	6.3
3	0.0773	0.0776	+0.3	4.3
4	0.0828	0.0828	0	6.3
5	0.0603[a]	0.0602	−0.1	0.6
6	0.0625	0.0628	+0.3	0.4
7	0.0590	0.0590	0	0.1
8	0.0603	0.0605	+0.2	0.4
9	0.0529	0.0525	−0.4	0.1

[a] Pptd. in 50% alcoholic solution.

Summary

1. Copper, lead, mercury, cadmium, bismuth and antimony are quantitatively precipitated by phenyl-thiohydantoic acid from a solution slightly acid with acetic acid.

2. Details are given for the separation of copper from the metals of the iron and zinc groups, with quantitative results for the separation from iron.

3. This method is especially adapted for small amounts of copper.